SYNTHESIS OF VINYL POLYMERS CONTAINING PHOSPHORUS

BY

JOHN COLLINS WRIGHT

B.S., West Virginia Wesleyan College, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1951

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Introduction

The properties of vinyl polymers are to a large extent dependent upon the functions attached to the carbon chain, and as a result, can be varied extensively by the introduction of even a small amount of a given function. The phosphonic acid group is a striking example of such a function. It contributes to vinyl polymers a marked resistance to burning and the hydrophylic nature of this group might introduce other properties where hydrogen bonding are concerned.

There are two general methods for preparing polymers containing phosphorus in the form of a phosphonic acid. The first procedure utilizes the synthesis and polymerization of phosphonic acids or esters containing a vinyl group. A limited number of these compounds have been studied, but the field is still largely undeveloped. The second and even lesser known method is the treatment of a preformed polymer in such a way as to introduce phosphorus into it.

The research presented in this thesis has for its purpose the synthesis and study of vinyl polymers containing phosphorus. It is designed to contribute to the existing knowledge about the effect of the phosphonic acid group on the properties of a polymer, and especially to supplement the available syntheses of such polymers.

Discussion Of Results

1-Phenylvinylphosphonic acid was synthesized and copolymerized with acrylonitrile and methyl methacrylate. The vinyl phosphonic acid entered the growing chains less readily than either of the other monomers, thus indicating that the phosphonic acid group does not activate a vinyl group for polymerization as strongly as other electron-withdrawing

functions.

Methyl 1-propene-2-phosphonate was synthesized and copolymerized with butadiene, styrene, methyl acrylate, methyl methacrylate, acrylonitrile and methyl vinyl ketone. The polymerizations were conducted in bulk, emulsion and solution systems, but in all cases the phosphonic acid ester entered the growing chains less readily than the monomer with which it was copolymerized. The phosphonic acid ester function does not activate a vinyl group for polymerization as strongly as most other electron-withdrawing functions. It is a better activating group than the phosphonic acid function. However this advantage may be due to solubility effects and not chemical in nature.

Methyl vinyl ketone was copolymerized with styrene, butadiene, methyl acrylate, methyl methacrylate and acrylonitrile to give polymers with a ketone function. Other copolymers which contained a carbonyl function were prepared by copolymerizing styrene with methyl isopropenyl ketone, methacrolein, cinnamaldehyde, benzalacetone and benzalacetophenone. This is the first time that the symetrically substituted olefins benzalacetone, benzalacetophenone and cinnamaldehyde have been copolymerized with styrene. The carbonyl groups in all of the copolymers prepared reacted with phosphorus trichloride in the presence of acetic acid (1) to give hydroxy phosphonic acid functions. Steric hindrance severely limited the reaction with phosphorus trichloride of the benzalacetone and benzalacetophenone copolymers. Solubility difficulties limited the same reaction with the acrylonitrile-methyl vinyl ketone copolymer. Otherwise the reaction of phosphorus trichloride was general for a ketone or aldehyde group in a polymer, and was a convenient reaction for introducing phosphonic acid functions into a polymer.

Copolymers of styrene and methyl vinyl ketone were treated with butoxydichlorophosphine and phenoxydichlorophosphine to give polymers with phosphonic acid half-ester functions. Treatment of the same copolymers with dibutoxy-

chlorophosphine and diphenoxychlorophosphine introduced phosphonic acid ester functions while use of phenyldichlorophosphine gave polymers which contained phosphinic acid functions.

A small amount of phosphorus was introduced as phosphonic acid groups into polystyrene by treatment with phosphorus trichloride and air (2).

The presence of phosphonic acid functions in polymers decreased their tendency to burn proportionally to the amount of phosphorus present. The polymers containing the phosphonic acid groups also had a tendency to cross link and become insoluble. The effect of the groups on the softening point of a polymer was not systematic, but when the group was introduced into copolymers their inherent viscosity decreased sharply.

BIBLIOGRAPHY

1. Conant, MacDonald and McB. Kinney, J. Am. Chem. Soc., 43, 1928 (1921).

2. Clayton and Jensen, J. Am. Chem. Soc., **70**, 3880 (1948).

VITA

The author was born on August 5, 1927 in Oak Hill, West Virginia. He attended public schools in Beckley, West Virginia and was graduated from Woodrow Wilson High School in May, 1944. He attended West Virginia Wesleyan College for one year, and then enlisted in the Navy Air Corps where he received further college training at the University of Michigan. After his release from the navy, he returned to West Virginia Wesleyan College and received the Bachelor of Science degree in Chemistry in 1948. At that time he entered the graduate school of the University of Illinois, where he was employed as a teaching assistant for two years. He held a University of Illinois Fellowship for September, 1950 to June, 1951.

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